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(54) A binderless storage phosphor screen with needle shaped crystals

(57) A binderless storage phosphor screen with needle shaped crystals, wherein the phosphor is an alkali halide phosphor and the needles show high [100] unit cell orientation in the plane of the screen.



FIG 1

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EP 1 113 458 A1

Description**FIELD OF THE INVENTION**

5 [0001] The present invention relates to a binderless storage phosphor screen with needle shaped phosphors.

BACKGROUND OF THE INVENTION

10 [0002] A well known use of storage phosphors is in the production of X-ray images. In **US-A 3 859 527** a method for producing X-ray images with a photostimulable phosphor, which are incorporated in a panel is disclosed. The panel is exposed to incident pattern-wise modulated X-ray beam and as a result thereof the phosphor temporarily stores energy contained in the X-ray radiation pattern. At some interval after the exposure, a beam of visible or infra-red light scans the panel to stimulate the release of stored energy as light that is detected and converted to sequential electrical signals which (are) be processed to produce a visible image. For this purpose, the phosphor should store as much as possible of the incident X-ray energy and emit as little as possible of the stored energy until stimulated by the scanning beam. This is called "digital radiography" or "computed radiography".

15 [0003] The image quality that is produced by any radiographic system using a phosphor screen thus also by a digital radiographic system, depends largely on the construction of the phosphor screen. Generally, the thinner a phosphor screen at a given amount of absorption of X-rays, the better the image quality will be. This means that the lower the ratio of binder to phosphor of a phosphor screen, the better the image quality, attainable with that screen, will be. Optimum sharpness can thus be obtained when screens without any binder are used. Such screens can be produced, e.g., by physical vapour deposition, which may be thermal vapour deposition, sputtering, electron beam deposition or other of phosphor material on a substrate. However, this production method can not be used to produce high quality screens with every arbitrary phosphor available. The mentioned production method leads to the best results when phosphor crystals with high crystal symmetry and simple chemical composition are used.

20 [0004] The use of alkali metal halide phosphors in storage screens or panels is well known in the art of storage phosphor radiology and the high crystal symmetry of these phosphors makes it possible to provide structured screens and binderless screens.

25 [0005] It has been disclosed that when binderless screens with an alkali halide phosphors are produced it is beneficial to have the phosphor crystal deposited as some kind of piles, needles, tiles, etc. In, e.g., **US-A-4 769 549** it is disclosed that the image quality of a binderless phosphor screen can be improved when the phosphor layer has a block structure shaped in fine pillars. In e.g. **US-A-5 055 681** a storage phosphor screen comprising an alkali halide phosphor in a pile-like structure is disclosed. The image quality of such screens needs still to be increased and in **JP-A-06/230 198** it is disclosed that the surface of the screen with pillar like phosphors is rough and that a levelling of that surface can increase the sharpness. In **US-A 5 874 744** the attention is drawn to the index of refractivity of the phosphor used to produce the storage phosphor screen with needle-like or pillar-like phosphor.

30 [0006] Although all screens disclosed in this prior art can yield X-ray images with good quality, the need for a better compromise between speed of the recording system (i.e. as low as possible patient dose) with an image with high sharpness and low noise is still there.

OBJECTS AND SUMMARY OF THE INVENTION

35 [0007] It is an object of the invention to provide a stimuable phosphor screen useful in an X-ray recording system with a very good compromise between speed of the recording system (i.e. as low as possible patient dose) with an image with high sharpness and low noise.

40 [0008] The above mentioned object is realised by providing a stimuable phosphor screen having the specific features defined in claim 1. Specific features for preferred embodiments of the invention are disclosed in the dependent claims.

45 [0009] Further advantages and embodiments of the present invention will become apparent from the following description and drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

50 [0010] Figure 1 shows a SEM photograph of a phosphor screen with needle-shaped phosphor.

[0011] Figure 2 shows an XRD-spectrum of a screen with a comparative needle-shaped phosphor.

55 [0012] Figures 3 - 6 show XRD spectra of screens with invention needle-shaped phosphors.

[0013] Figure 7 shows a schematic view of a vapour deposition apparatus useful for producing a binderless storage phosphor screen.

DETAILED DESCRIPTION OF THE INVENTION

[0014] It has now been found that it is possible to improve a binderless phosphor screen comprising an alkali halide phosphor by producing it in such a manner that the phosphor is present on the support as needle-like crystals having a specific crystal orientation. It has been found that, when a phosphor screen showing high (100) unit cell orientation in the plane of the screen was produced, that such a screen shows a better compromise between speed and sharpness. The phosphor screens showing high (100) unit cell orientation in the plane of said screen are characterised by an XRD-spectrum wherein the intensity of the (100) diffraction line is at least equal to the intensity of the (110) diffraction line, when said XRD-spectrum is measured by positioning an X-ray source and an X-ray diffraction intensity detector at equal but varying angles with respect to the normal to said screen. Preferably the intensity of the (100) diffraction line is at least 5 times higher than the intensity of the (110) diffraction line and most preferably the intensity of the (100) diffraction line is at least 10 times higher than the intensity of the (110) diffraction line.

[0015] To realise such a crystal orientation on the screen the binderless phosphor layer is applied to the support by a method selected from the group consisting of physical vapour deposition, thermal vapour deposition, chemical vapour deposition, electron beam deposition, radio frequency deposition and pulsed laser deposition. In fact any of the methods above for preparing the binderless phosphor screen is suitable as long as the parameters of the method can be adjusted so that the requirements of the crystallinity of the phosphor needles as described herein above are met. Preferably the binderless phosphor screen is prepared by vacuum deposition under an inert gas atmosphere. It was found that by adjusting the temperature of the substrate and the pressure of the inert gas during vacuum deposition, the crystal orientation of the needles could be adjusted to the desired level.

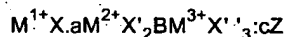
[0016] The inert gas that is used during vapour deposition is preferably Ar. The temperature of the gas stream that enters the vacuum deposition apparatus is kept between 0 °C and 100 °C. Preferably the gas stream is kept at room temperature, i.e., between about 20 °C and about 30 °C. The cool gas stream entering the vacuum deposition apparatus can cool both the vapour before it is deposited as well as the substrate. It is preferred to keep said substrate at a temperature, T, so that 50 °C ≤ T ≤ 300 °C, preferably 90 °C ≤ T ≤ 200 °C. The Ar-pressure is at most 10 Pa, preferably kept between 1 Pa and 3 Pa, both limits included. In a more preferred embodiment the Ar-pressure is kept between 0.20 and 2.00 Pa and the temperature is adjusted so that the product between temperature in degrees Celsius and Ar-pressure in Pa is between 20 and 350.

[0017] It was found that when a phosphor screen was prepared under the circumstances set out above not only the crystal orientation of the needles could be adjusted to the desired level, but also the macroscopic dimensions of the needles could be influenced: when a method described above was used, very thin needles were obtained. This was especially so when the rate of vapour deposition of the phosphor or phosphor precursors was above 1 mg/cm²min.

[0018] Figure 7 shows a schematic view of a vapour deposition apparatus useful for producing a binderless storage phosphor screen comprising an alkali metal storage phosphor said screen showing an XRD-spectrum with a (100) diffraction line having an intensity I₁₀₀ and a (110) diffraction line having an intensity I₁₁₀, so that I₁₀₀/I₁₁₀ ≥ 1, when said XRD-spectrum is measured according to TEST A. Such apparatus comprises a vacuum vessel (1) in which a vapour deposition source (2) is arranged opposite the substrate (4), which preferably rotates about an axis (3). An inert gas, such as argon, which is very much cooler than the vapour temperature of, typically, 650 to 700 °C, for example being at room temperature, can be introduced into the vacuum vessel (1) via a regulating valve (5); the inert gas preferably firstly impinges on a baffle plate (6) and is not introduced directly into the vapour jet (7). The inert gas is evacuated up again via a vacuum pump (8), the vacuum pump is set such that a pressure of less than 10 Pa, preferably between 1 Pa and 3 Pa, is produced within the vacuum vessel (1). If so desired, when the cool gas stream is not sufficient for cooling of the substrate, it is possible to couple the substrate (4) to an external cooling device (not shown).

[0019] A binderless phosphor screen according to this invention can be prepared by vacuum deposition of the phosphor crystals on the substrate as well as by combining (mixing) the ingredients for the phosphor (phosphor precursors) and then evaporating this mixture so as to have the phosphor formed in situ during evaporation.

[0020] The phosphor in a binderless phosphor screen according to this invention can be any alkali metal phosphor known in the art. Suitable phosphors are, e.g., phosphors according to formula I:



wherein: M¹⁺ is at least one member selected from the group consisting of Li, Na, K, Cs and Rb,

M²⁺ is at least one member selected from the group consisting of Be, Mg, Ca, Sr, Ba, Zn, Cd, Cu, Pb and Ni;

M³⁺ is at least one member selected from the group consisting of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Al, Bi, In and Ga,

Z is at least one member selected from the group Ga¹⁺, Ge²⁺, Sn²⁺, Sb³⁺ and As³⁺, X, X' and X'' can be the same or different and each represents a halogen atom selected from the group consisting of F, Br, Cl, I and 0 ≤ a ≤ 1, 0 ≤ b ≤ 1.

1 and $0 < c \leq 0.2$. Such phosphors have been disclosed in, e.g., US-A-5 736 069.

[0021] Highly preferred phosphors for use in a binderless phosphor screen of this invention are CsX:Eu stimuable phosphors, wherein X represents a halide selected from the group consisting of Br and Cl prepared by a method comprising the steps of:

- mixing said CsX with between 10^{-3} and 5 mol % of an Europium compound selected from the group consisting of EuX_2 , EuX_3 and EuOX , X' being a member selected from the group consisting of F, Cl, Br and I,
- firing said mixture at a temperature above 450°C
- cooling said mixture and
- recovering the CsX:Eu phosphor.

[0022] Most preferably a CsBr:Eu stimuable phosphor, is used prepared by a method comprising the steps of:

- mixing said CsX with between 10^{-3} and 5 mol % of an Europium compound selected from the group consisting of EuX_2 , EuX_3 and EuOX , X' being a member selected from the group consisting of F, Cl, Br and I,
- firing said mixture at a temperature above 450°C
- cooling said mixture and
- recovering the CsX:Eu phosphor.

[0023] The binderless screen can be prepared by bringing the finished phosphor on the support by any method selected from the group consisting of (physical vapour deposition is de verzamelnaam voor thermal vapour deposition, electron beam vapour deposition, sputtering, ...), thermal vapour deposition, chemical vapour deposition, electron beam deposition, radio frequency deposition and pulsed laser deposition. It is also possible to bring the alkali metal halide and the dopant together and depositing them both on the support in such a way that the alkali metal phosphor is doped during the manufacture of the screen. Thus the invention encompasses a method for manufacturing a phosphor screen containing a CsX:Eu stimuable phosphor, wherein X represents a halide selected from the group consisting of Br and Cl comprising the steps of:

- bringing multiple containers of said CsX and an Europium compound selected from the group consisting of EuX_2 , EuX_3 and EuOX , X' being a halide selected from the group consisting of F, Cl, Br and I in condition for vapour deposition and
- depositing, by a method selected from the group consisting of, thermal vapour deposition, chemical vapour deposition, electron beam deposition, radio frequency deposition and pulsed laser deposition, both said CsX and said Europium compound on a substrate in such a ratio that on said substrate a CsX phosphor, doped with between 10^{-3} and 5 mol % of Europium, is formed.

[0024] The deposition can proceed from a single container containing a mixture of the starting compounds in the desired proportions. Thus the method encompasses further a method for manufacturing a phosphor screen containing a CsX:Eu stimuable phosphor, wherein X represents a halide selected from the group consisting of Br and Cl comprising the steps of:

- mixing said CsX with between 10^{-3} and 5 mol % of an Europium compound selected from the group consisting of EuX_2 , EuX_3 and EuOX , X' being a halide selected from the group consisting of F, Cl, Br and I
- bringing said mixture in condition for vapour deposition and
- depositing said mixture on a substrate by a method selected from the group consisting of physical vapour deposition, thermal vapour deposition, chemical vapour deposition, electron beam deposition, radio frequency deposition and pulsed laser deposition.

[0025] Support materials useful for binderless storage screens having a phosphor layer with a crystal orientation as per this invention include cardboard, glass, plastic films such as films of cellulose acetate, polyvinyl chloride, polyvinyl acetate, polyacrylonitrile, polystyrene, polyester, polyethylene terephthalate, polyamide, polyimide, cellulose triacetate and polycarbonate; metal sheets such as aluminium foil and aluminium alloy foil; ordinary papers; baryta paper; resin-coated papers; pigment papers containing titanium dioxide or the like; and papers sized with polyvinyl alcohol or the like. A glass or Al-sheet or a thermostable plastic film is preferably employed as the support material.

[0026] When a glass support is used the support may comprise a coated layer with a light absorbing compound. This layer can be present on the back side (side where no phosphor is present) or may be present underneath the phosphor. The supports can also comprise subbing layers for having a better adhesion between the phosphor and the support.

[0027] The support, when it is a thermostable plastic film may contain a light-absorbing material such as carbon black, or may contain a light-reflecting material such as titanium dioxide or barium sulphate. The former is appropriate for preparing a high-resolution type storage screen, while the latter is appropriate for preparing a high-sensitivity type storage screen.

5 [0028] These supports may have a thickness which may differ depending on the material of the support, and may generally be between 60 μm and 10,000 μm , more preferably between 80 μm and 5,000 μm from the standpoint of handling.

10 EXAMPLES

Preparation of the phosphor

[0029] CsBr:Eu screens were made via thermal vapour deposition of CsBr and EuOBr. To this aim, CsBr was mixed with EuOBr and placed in a container in a vacuum deposition chamber. The phosphor was deposited on a glass disk with a thickness of 1.5 mm and a diameter of 40 mm. The distance between the container and the substrate was 10 cm. During evaporation, the substrate was rotated at 12 rpm. The container with starting materials was heated to a temperature of 750°C.

Before the start of the evaporation, the chamber was evacuated to a pressure of $4 \cdot 10^{-5}$ mbar. During the evaporation process, Ar was introduced in the chamber. Variables in the deposition process were the substrate temperature and the Ar gas pressure. The different screens were produced under the conditions listed in Table 1. The Eu-concentration in the evaporated screens was measured with X-ray fluorescence and was of the order of 800 ppm.

Via Scanning Electron Microscopy (SEM), the morphology of the deposited phosphor layer was determined. All phosphor layers were made up of needle shaped crystals.

Figure 1 shows a SEM view of an example phosphor layer taken perpendicular on an edge of the phosphor layer. It is clear that a needle like structure is present.

Table 1:

Substrate temperature and Ar gas pressure at the different screen depositions		
Screen	Substrate temperature (°C)	Ar pressure (Pa)
Comparative example 1	130	3.2
Invention Example 1	150	2.2
Invention Example 2	150	1.1
Invention Example 3	300	0
Invention Example 4	92	2.4

Measurement of crystal orientation : TEST A

[0030] The orientation of the crystal unit cell in the deposited needle shaped crystal has been determined through measurement of the XRD spectrum. XRD spectra have been measured with the commercially available diffractometer. The diffractometer was a Philips X'pert with a MPPS (Multiple Purpose Sampling Stage) and a Cu tube emitting a $K\alpha$ -line of 0.154056 nm. The spectra were taken and analysed with the commercial software coming with the diffractometer. The settings and measurement parameters of the measurement were as follows (TEST A):

Settings 40 kV en 50 mA

Incident beam : Divergence slit : fixed $1/8^\circ$
Incident beam : Anti scatter slit : fixed $1/4^\circ$
Incident beam : Fixed beam mask : 10mm

Measurement Start 2θ : 2.00°
parameters End 2θ : 80.00°

Step size : 0.05°
Time per step : 0.60s

Secondary beam path : lower
 Scan axis : 2 θ
 Scan mode : continuous
 Total time : 15min36s
 Gonio angle : 2.0°
 Spinning : no

[0031] Figure 2 shows the XRD spectrum comparative example 1. A fairly strong [100] diffraction line is shown at 2 θ of about 21° and an evenly strong [110] diffraction line is shown at 2 θ of about 29°, also a strong [200] diffraction line is shown at 2 θ of about 42°.

[0032] Figures 3 to 6 show the XRD-spectra of respectively invention example 1, 2, 3 and 4. In these spectra the [110] diffraction line at 2 θ of about 29° is barely visible, while the [100] diffraction line at 2 θ of about 21° and the [200] diffraction line at 2 θ of about 42° remain very strong.

[0033] For each of the screens, the ratio between the intensity of the [100] peak in the XRD-spectrum and the [110] peak was calculated. The results are given in table 2

Table 2

Screen	Ratio [100]/[110]
Comparative example 1	0.79
Invention Example 1	54.71
Invention Example 2	52.65
Invention Example 3	12.16
Invention Example 4	14.05

Sensitivity and sharpness measurements

[0034] In a first measurement the sensitivity (speed) of the phosphor screens, prepared under the conditions given in Table 1 was measured.

[0035] The screens were homogeneously irradiated with a dose of ca. 50 mR at 80 kVp. Read out was done in a flying spot scanner. In the scanner, the scanning light source was a 30 mW diode laser emitting at 690 nm. A 4-mm BG-39 (trade name of Hoya) filter was used to separate the stimulation light from the screen emission light. The scan-average levels (SAL's) were determined as the average signal produced by the screens in the photomultiplier tube.

[0036] In a second measurement, the sharpness of the images, produced by the screens was measured. As a measure for the sharpness, the square wave response at 2 lp/mm was determined.

[0037] A grid with line pairs at spatial frequencies of 0.025 to 3 lp/mm was placed on top of the cassette, containing the screens. The grid was imaged at 80 kVp and 5 mA during 30". The screens were scanned with the flying spot scanner described above. The signal modulation was determined at 0.025 lp/mm and at 2 lp/mm. The SWR at 2 lp/mm was calculated as the ratio of the signal modulation at 2 lp/mm to the signal modulation at 0.025 lp/mm. The results of the measurements are listed in Table 3. Wherein the speed of the comparative example screen is arbitrary set to 100.

Table 3

Screen	Speed (arbitrary units)	SWR at 2 lp/mm
Comparative example 1	100	0.50
Invention Example 1	186	0.56
Invention Example 2	214	0.59
Invention Example 3	102	0.66
Invention Example 4	156	0.53

[0038] It can be concluded that the comparative example 1 screen with less developed (100) unit cell orientation, has inferior quality with respect to the invention examples 1 - 4 with almost perfect (100) unit cell orientation. It is possible to adjust the orientation of the crystal to choose a desired speed/sharpness compromise by using the temperature of the substrate during the vacuum deposition and the pressure of the inert gas as parameters.

Claims

1. A binderless storage phosphor screen comprising an alkali metal storage phosphor characterised in that said screen shows an XRD-spectrum with a (100) diffraction line having an intensity I_{100} and a (110) diffraction line having an intensity I_{110} , so that $I_{100}/I_{110} \geq 1$, when said XRD-spectrum is measured according to TEST A.
2. A binderless storage phosphor screen according to claim 1, wherein $I_{100}/I_{110} \geq 5$.
3. A binderless storage phosphor screen according to claim 1 or 2, wherein said phosphor is an alkali metal phosphor.
4. A binderless storage phosphor screen according to claim 1 or 2, wherein said phosphor is a CsX:Eu stimuable phosphor, wherein X represents a halide selected from the group consisting of Br and Cl is used, prepared by a method comprising the steps of :
 - mixing said CsX with between 10^{-3} and 5 mol % of an Europium compound selected from the group consisting of EuX_2 , EuX_3 and EuOX , X' being a member selected from the group consisting of F, Cl, Br and I,
 - firing said mixture at a temperature above 450°C
 - cooling said mixture and
 - recovering the CsX:Eu phosphor.
5. A binderless storage phosphor screen according to any of claims 1 to 3, containing a CsX:Eu stimuable phosphor, wherein X represents a halide selected from the group consisting of Br and Cl wherein said screen is prepared by a method comprising the steps of :
 - mixing said CsX with between 10^{-3} and 5 mol % of an Europium compound selected from the group consisting of EuX_2 , EuX_3 and EuOX , X' being a halide selected from the group consisting of F, Cl, Br and I
 - bringing said mixture in condition for vapour deposition and
 - depositing said mixture on a substrate by a method selected from the group consisting of physical vapour deposition, thermal vapour deposition, chemical vapour deposition, electron beam deposition, radio frequency deposition and pulsed laser deposition.
6. Method for producing a binderless storage phosphor screen comprising the steps of :
 - providing an alkali metal storage phosphor
 - vacuum depositing said phosphor on a substrate characterised in that during said step of vacuum depositing said substrate is kept at a temperature T, such that $50^\circ\text{C} \leq T \leq 300^\circ\text{C}$ and said vacuum deposition proceeds in an Ar-atmosphere with an Ar-pressure of at most 3 Pa.
7. Method for producing a binderless storage phosphor screen comprising the steps of :
 - combining phosphor precursors for an alkali metal storage phosphor
 - vacuum depositing said combination of phosphor precursors on a substrate characterised in that during said step of vacuum depositing said substrate is kept at a temperature T, such that $50^\circ\text{C} \leq T \leq 300^\circ\text{C}$ and said vacuum deposition proceeds in an Ar-atmosphere with an Ar-pressure of at most 3 Pa.
8. A method according to claim 6 or 7, wherein said temperature of said substrate T, is such that $90^\circ\text{C} \leq T \leq 200^\circ\text{C}$
9. A method according to any of claims 6 to 8, wherein said Ar-pressure is kept between 0.20 and 2.00 Pa, both limits included and said temperature of said substrate is adjusted so as to have a product between temperature, in degree Celsius, and Ar-pressure, in Pa, between 20 and 350, both limits included.
10. A method according to any of claims 6 to 10, wherein during said step of vacuum deposition a deposition rate of at least $1\text{ mg/cm}^2\text{min}$ is used.

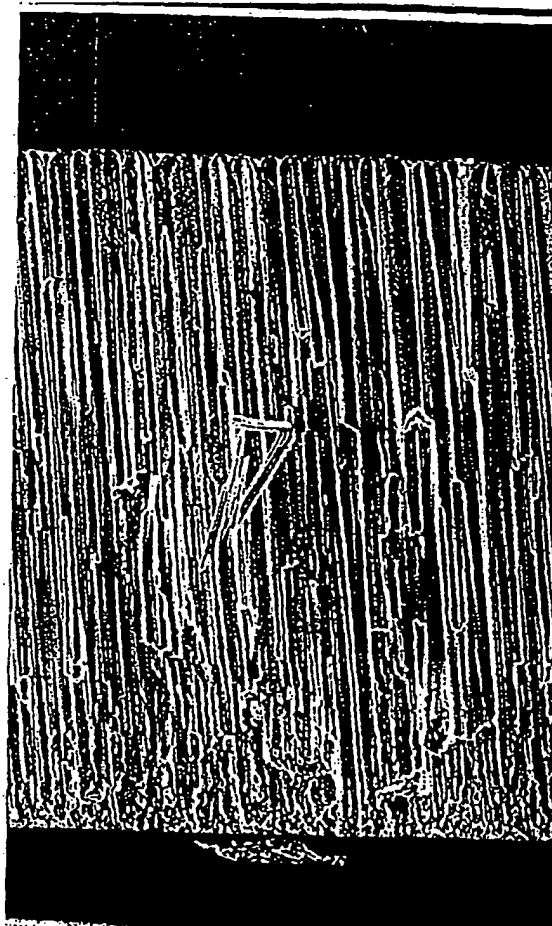


FIG 1

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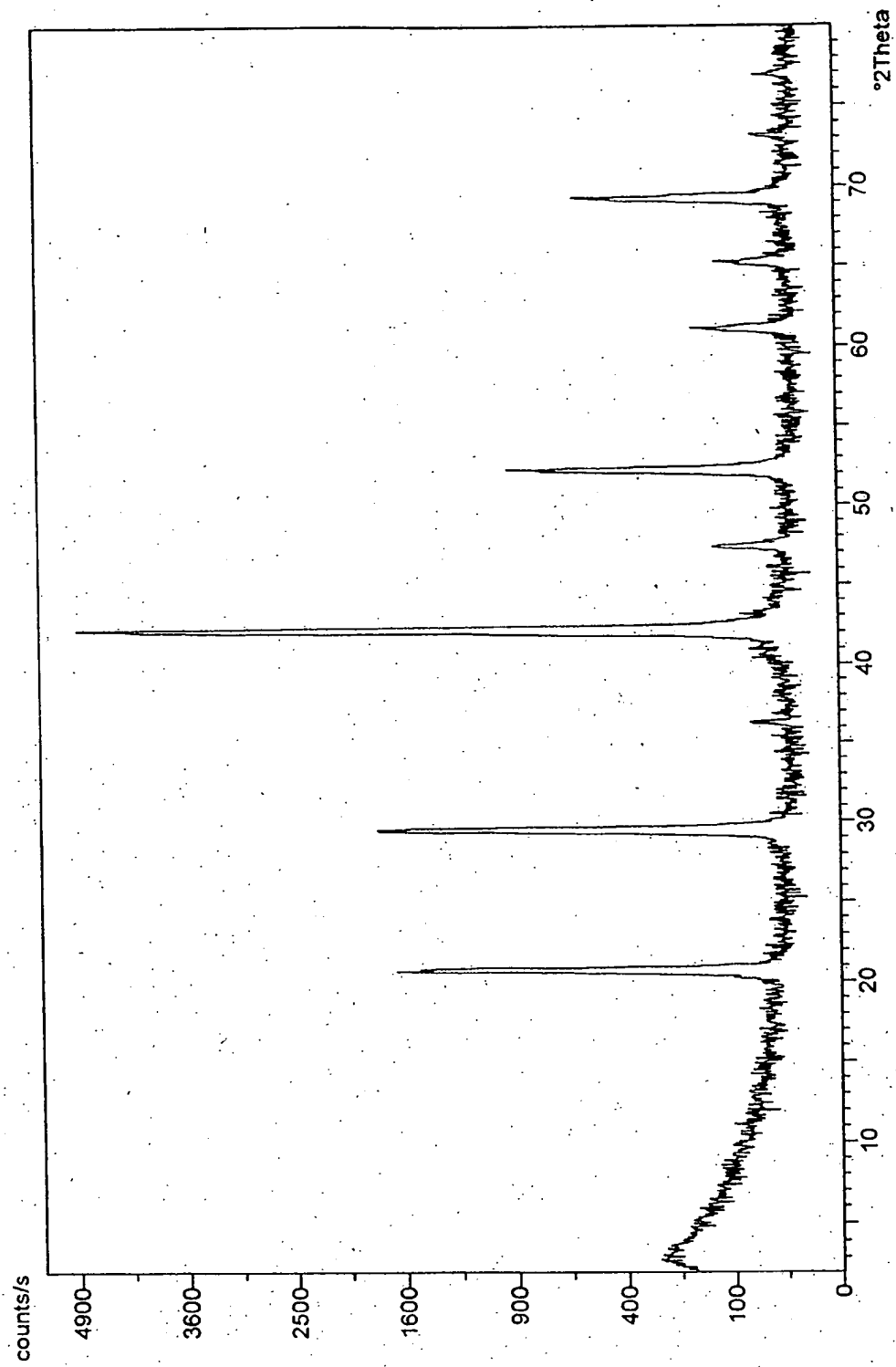


FIG 2

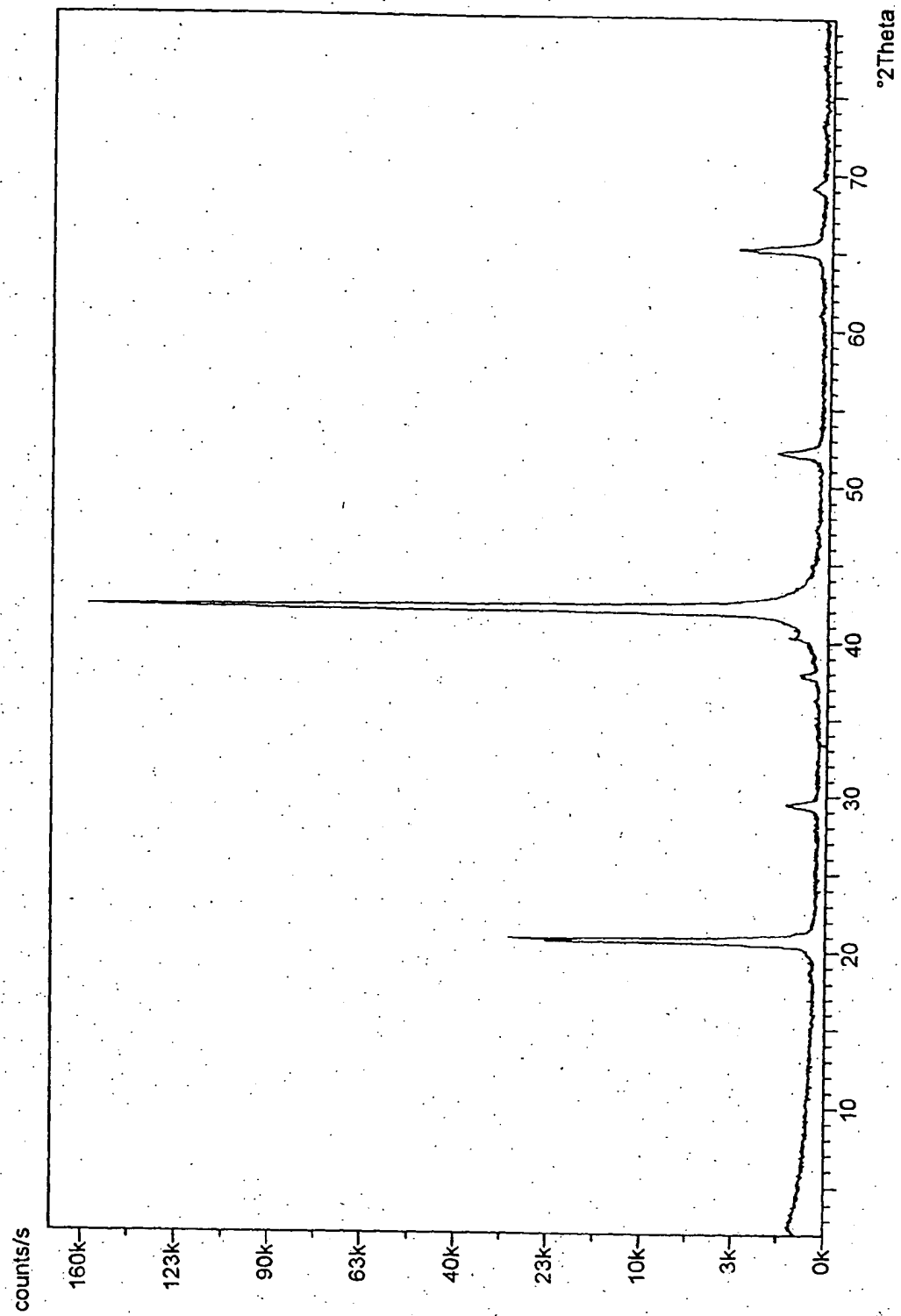


FIG 3

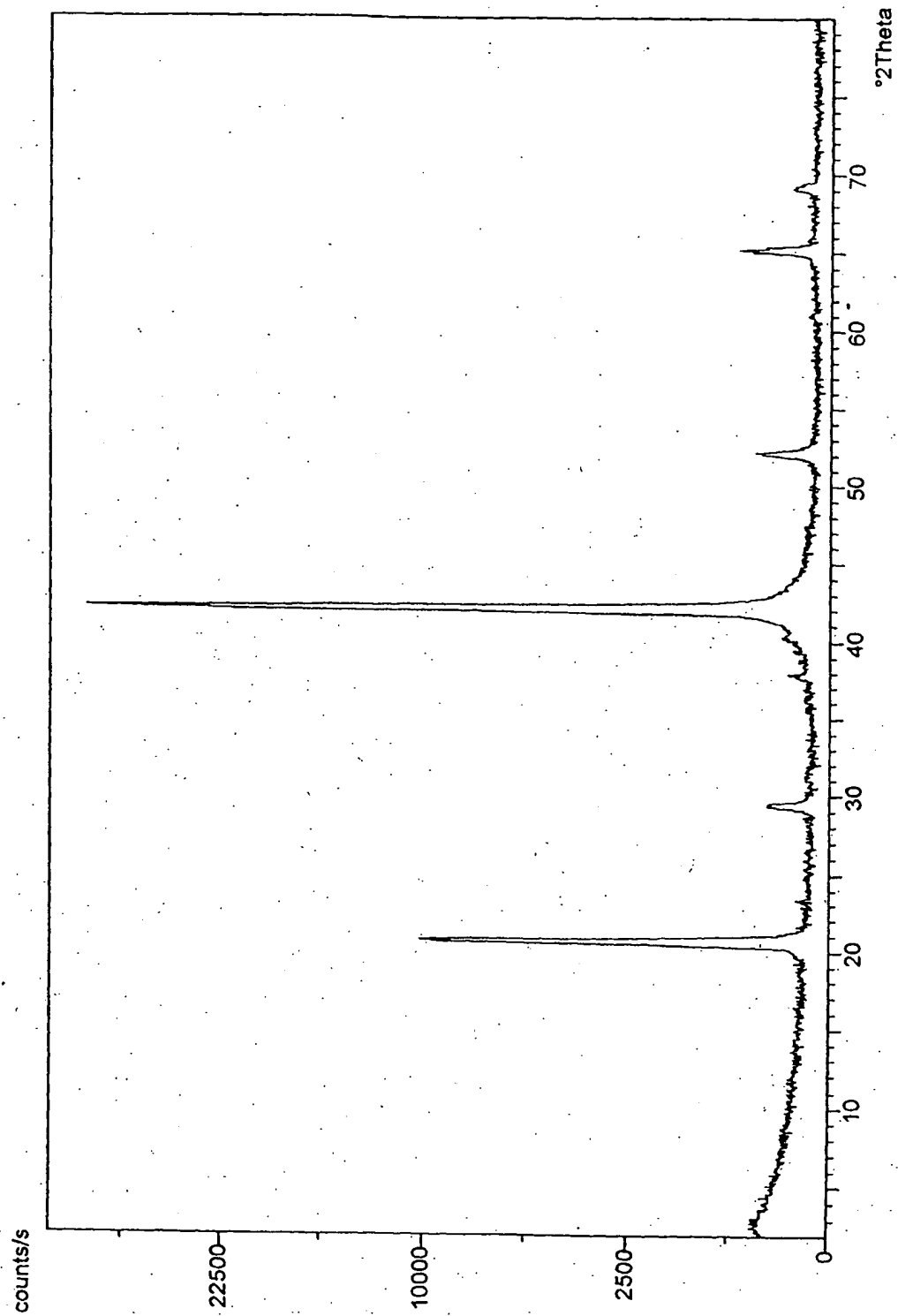


FIG 4

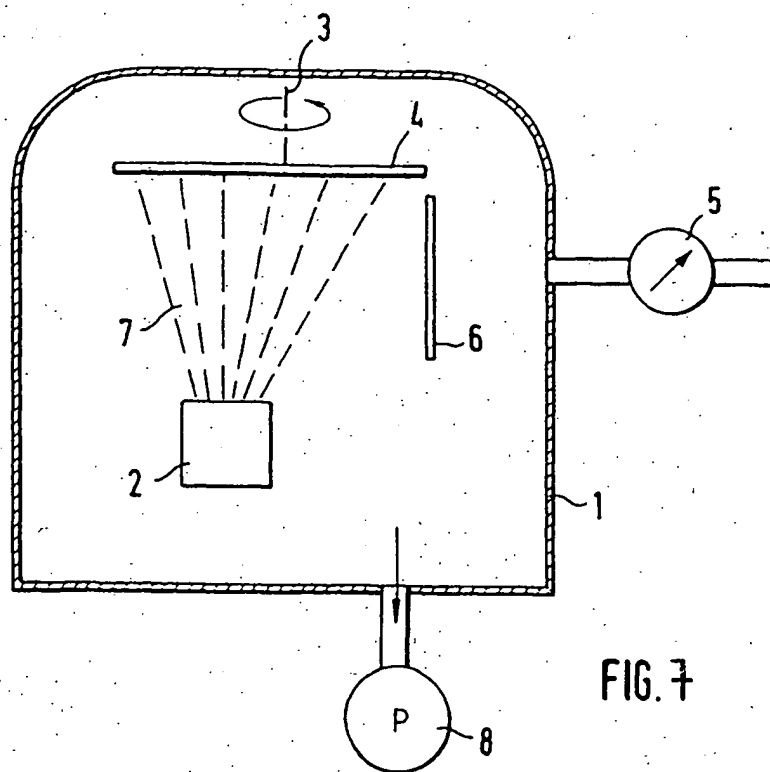


FIG. 7



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EUROPEAN SEARCH REPORT

Application Number
EP 00 20 4217

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	EP 0 352 152 A (THOMSON CSF) 24 January 1990 (1990-01-24) * the whole document *	1,3-5	621K4/00 C09K11/85
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			G21K C09K
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 16 March 2001	Examiner Drouot-Onillon, M-C
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
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ON EUROPEAN PATENT APPLICATION NO.**

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(54) Title: METHOD FOR PREPARING A CsX PHOTOSTIMULABLE PHOSPHOR AND PHOSPHORS THEREFROM

(57) Abstract: A CsX:Eu phosphor produced by heating a cesium halide with a Europium compound containing one or more halides selected from the group consisting of F, Cl, Br and I. Preferably the Europium compound is selected from the group consisting of EuX₂, EuX₃ and EuOX, X' being one or more halides selected from the group consisting of F, Cl, Br and I. The invention also includes novel phosphors having properties inherent to the manufacturing process as well as other phosphors containing a mixture of Br and Cl in the cesium halide, europium doped phosphor. A method for preparing a binderless phosphor screen using these phosphors and a method for recording and reproducing an X-ray image using such screens are also disclosed.

**METHOD FOR PREPARING A CsX PHOTOSTIMULABLE PHOSPHOR AND
PHOSPHORS THEREFROM**

5 This application claims the benefit of U.S. Provisional Patent Application No. 60/142,276, filed July 2, 1999 and U.S. Provisional Patent Application No. 60/159,004, filed October 8, 1999, both of which are incorporated herein by reference for all purposes.

BACKGROUND OF THE INVENTION

10 **Field of the Invention**

 The present invention relates to a method for recording and reproducing images of objects made by high energy radiation. It relates especially to a method for manufacturing a cesium halide storage phosphor, particular phosphors and a storage phosphor panel containing them.

15 **Discussion**

 A well-known use of phosphors is in the production of X-ray images. In a conventional radiographic system an X-ray radiograph is obtained by X-rays transmitted image-wise through an object and converted into light of corresponding intensity in a so-called intensifying screen (X-ray conversion screen) wherein phosphor particles absorb the transmitted X-rays and
20 convert them into visible light and/or ultraviolet radiation to which a photographic film is more sensitive than to the direct impact of X-rays.

 According to another method of recording and reproducing an X-ray pattern disclosed e.g., in U.S. Patent No. 3,859,527 a special type of phosphor is used, known as a photostimulable phosphor, which being incorporated in a panel, is exposed to incident pattern-
25 wise modulated X-ray beam and as a result thereof temporarily stores energy contained in the X-ray radiation pattern. At some interval after the exposure, a beam of visible or infra-red light scans the panel to stimulate the release of stored energy as light that is detected and converted

to sequential electrical signals which are can be processed to produce a visible image. For this purpose, the phosphor should store as much as possible of the incident X-ray energy and emit as little as possible of the stored energy until stimulated by the scanning beam. This is called "digital radiography" or "computed radiography".

5 The image quality that is produced by a conventional as well as by a digital radiographic system depends largely on the construction of the phosphor screen. Generally, the thinner a phosphor screen at a given amount of absorption of X-rays, the better the image quality will be. This means that the lower the ratio of binder to phosphor of a phosphor screen, the better the image quality, attainable with that screen, will be. Optimum sharpness can thus
10 be obtained when screens without any binder are used. Such screens can be produced, e.g., by physical vapor deposition, which may be thermal vapor deposition, sputtering, electron beam deposition or other of phosphor material on a substrate. However, this production method can not be used to produce high quality screens with every arbitrary phosphor available. The mentioned production method leads to the best results when phosphor crystals with high crystal
15 symmetry and simple chemical composition are used. Phosphors having complicated crystal structures as, e.g., alkaline earth fluorohalides, tend to decompose (partially) under physical vapor deposition and the production of screens in this way while using phosphors with complicated crystal structure is quasi impossible and leads to sub-optimal results. The use of alkali metal halide phosphors in storage screens or panels is well known in the art of storage
20 phosphor radiology and the high crystal symmetry of these phosphors makes it possible to provide structured screens and binderless screens. In e.g., U.S. Patent No. 5,055,681 a storage phosphor screen comprising an alkali metal phosphor in a pile-like structure is disclosed.

In U.S. Patent No. 5,736,069 an alkali metal storage phosphor is disclosed corresponding to the formula : $M^{1+}X_aM^{2+}X'_2bM^{3+}X''_3cZ$

25 wherein: M^{1+} is at least one member selected from the group consisting of Li, Na, K, Cs and Rb,

M^{2+} is at least one member selected from the group consisting of Be, Mg, Ca, Sr, Ba, Zn, Cd, Cu, Pb and Ni,

30 M^{3+} is at least one member selected from the group consisting of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Al, Bi, In and Ga,

Z is at least one member selected from the group Ga^{1+} , Ge^{2+} , Sn^{2+} , Sb^{3+} and As^{3+} ,

X, X' and X'' can be the same or different and each represents a halogen atom selected from the group consisting of F, Br, Cl, and I, and $0 \leq a \leq 1$, $0 \leq b \leq 1$ and $0 < c \leq 0.2$.

In EP-A-174 875 and EP-B-252 991 (and U.S. Patent No. 5,028,509), amongst other alkali metal stimuable phosphors a CsBr:Eu phosphor is disclosed, wherein the Eu is
5 incorporated in the CsBr by firing CsBr with Europium oxide.

The alkali metal phosphors according to the disclosures mentioned above find applications for preparing structured screens and binderless screens, it would, nonetheless, be advantageous to have CsX phosphor with enhanced speed.

10

SUMMARY OF THE INVENTION

It is a first object of the invention to provide a method for producing a novel cesium halide phosphor, where such phosphor exhibits a high speed and thus provides more degrees of freedom for producing storage phosphor panels that combine high speed with high resolution.

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It is a second object of the invention to provide a panel, containing cesium halide phosphor that exhibits a high speed combined with a high resolution.

It is a third object of the invention to provide a method for recording and reproducing images of objects made by high energy radiation.

20

Further objects and advantages of the invention will become clear from the detailed description hereinafter. All references cited are incorporated by reference.

The object of the invention is realized by providing a method for manufacturing a CsX:Eu stimuable phosphor, wherein X represents a halide selected from the group consisting of Br, Cl and combinations thereof comprising the steps of:

25

- mixing or otherwise combining the CsX with between 10^{-3} mol % and 5 mol % of a Europium compound, relative to the moles of CsX, the Europium compound being selected from the group consisting of EuX'_2 , EuX'_3 and EuOX' , X' being one or more halide selected from the group consisting of F, Cl, Br and I;

- heating (e.g., firing) said mixture at a temperature above about 450 °C; and
- cooling said mixture.

Typically, the resulting CsX:Eu phosphor is recovered from the crucible or other suitable container in which it was prepared. The CsX:Eu phosphor resulting from such methods is novel, and provides substantial practical advantages over known CsX:Eu phosphors.

The second object of the invention is realized by manufacturing a phosphor screen
5 containing a CsX:Eu stimuable phosphor, wherein X represents a halide selected from the group consisting of Br, Cl and combinations thereof comprising the steps of:

- preparing said CsX:Eu phosphor by heating (e.g., firing) a mixture of said CsX with
between 10^{-3} mol % and 5 mol % of an Europium compound selected from the group
consisting of EuX'_2 , EuX'_3 and EuOX' , X' being one or more halide selected from the group
10 consisting of F, Cl, Br and I; and

- applying said phosphor on a substrate by a method selected from the group
consisting of chemical vapor deposition or physical vapor deposition, including thermal
vapor deposition, electron beam evaporation, magnetron sputtering, radio frequency
sputtering and pulsed laser deposition or atomization techniques such as spray drying,
15 thermal spraying, etc.

The second object of the invention is also realized by manufacturing a phosphor
screen containing a CsX:Eu stimuable phosphor, wherein X represents a halide selected from
the group consisting of Br, Cl and combinations thereof comprising the steps of:

- bringing multiple containers of said CsX and an Europium compound selected from
20 the group consisting of EuX'_2 , EuX'_3 and EuOX' , X' being one or more halide selected from
the group consisting of F, Cl, Br and I in condition for vapor deposition; and

- depositing, by a method selected from the group consisting of chemical vapor
deposition or physical vapor deposition, including thermal vapor deposition, electron beam
evaporation, magnetron sputtering, radio frequency sputtering and pulsed laser deposition or
25 atomization techniques such as spray drying, thermal spraying, etc, both said CsX and said
Europium compound on a substrate in such a ratio that on said substrate a CsX phosphor,
doped with between 10^{-3} mol % and 5 mol % of an Europium compound, is formed.

The third object of the invention is realized by providing a method for recording and
reproducing images of objects made by high energy radiation comprising the steps of:

30 - exposing a panel containing a CsX:Eu stimuable phosphor, wherein X represents a
halide selected from the group consisting of Br, Cl and combinations thereof, including
between 10^{-3} mol % and 5 mol % of a Europium dopant; said dopant originating from a

Europium compound selected from the group consisting of EuX'_2 , EuX'_3 and EuOX' , X' being one or more halide selected from the group consisting of F, Cl, Br and I, with X-ray radiation for storing energy in said phosphor,

- stimulating said panel with stimulating radiation having a wavelength between 500 nm and 1100 nm, releasing said stored energy as stimulated radiation and
- collecting said stimulated radiation.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows the emission spectrum of an invention CsBr:Eu phosphor.

Fig. 2 shows the stimulation spectrum of an invention CsBr:Eu phosphor.

Fig. 3 shows the conversion efficiency of the CsBr:Eu phosphors as a function of the concentration and the type of dopant.

Fig. 4 shows the ultra-violet excited (280 nm) luminescence spectrum recorded from a film of europium doped cesium bromide.

DETAILED DESCRIPTION

In this document the term "X-ray" has to be understood as any penetrating radiation and includes irradiation originating from a radioisotope (e.g. Co60, Ir192, Se75, etc.), radiation created by an X-ray generator of any type, radiation and high energy particles created by a high energy radiation generator (e.g. Betatron), and/or radiation from a sample labeled with a radioisotope as is the case of, e.g., autoradiography.

Conventional wisdom in the art of producing stimuable phosphors teaches that when doping a phosphor, e.g. BaFBr, with Eu-ions, it does not matter under what form the Eu-ions are mixed with the raw mix before firing. It is accepted that oxides of trivalent and divalent europium can be used as well as halides of trivalent and divalent europium and that the same phosphor quality will be obtained.

Also in EP-A-174 875 there is no teaching that in the manufacturing of alkali metal halide phosphors the use of different Europium compounds for doping the alkali metal halide would give phosphors with different quality or enhanced qualities (e.g., enhanced properties).

When studying the examples of EP-A-174 875 it seems that only Eu_2O_3 is a suitable compound for doping a simple CsBr phosphor.

It was now surprisingly found that a CsX:Eu phosphor could be produced in the manner disclosed herein, and that such phosphor exhibits much higher speed than the prior art CsX:Eu phosphor. The CsX:Eu phosphor of the present invention is prepared by using as an Eu dopant in the raw mix a Europium compound selected from the group consisting of EuX'_2 , EuX'_3 and EuOX' , where X' is one or more halide selected from the group consisting of F, Cl, Br and I. Especially the use of EuBr_3 , EuBr_2 , EuCl_2 and EuOBr gave very good results. This result was even more surprising when consideration is given to the observation that when doping a CsBr phosphor with Tl, better performance was achieved using Tl_2O instead of TlBr .

The Europium compound selected from the group consisting of EuX'_2 , EuX'_3 and EuOX' , X' being one or more halide selected from the group consisting of F, Cl, Br and I, is preferably mixed with the CsX in such a way that between 10^{-3} mol % and 5 mol % of the Europium compound is present, relative to the number of moles of CsX. Preferably said Europium compound is mixed with the CsX in such a way that between 10^{-1} mol % and 3 mol % of the Europium compound is present relative to the CsX. These starting materials are combined and/or intimately mixed by suitable methods known in the art.

The combined starting materials are preferably heated (e.g., fired) at a temperature ranging from about 450°C to about 1000°C , more preferably at a temperature ranging from about 550°C to about 1000°C , and still more preferably at a temperature ranging from about 650°C to about 1000°C and most preferably at a temperature of about 700°C . The dwell time at the firing temperature is not critical, and can range from about 1 minute to about 10 hours, from about 5 minutes to about 6 hours or from about 5 minutes to about 1 hour. The combined starting materials are most preferably heated to a temperature (e.g., fired at temperatures) above the melting point of CsBr. The heated mixture can be cooled by methods known in the art. Cooling rates can be typical of those employed in the art and can vary based on the method of cooling.

In addition the phosphors of the present invention include a mixture of halides in the formula CsX_aEu , where X is a mixture of Br and Cl. This results in a phosphor of the formula $\text{CsBr}_a\text{Cl}_b\text{Eu}$ where $a + b = 1$, a and b are each numbers and a ranges from about 0.99

to about 0.8 and b ranges from about 0.01 to about 0.2. Preferably, a ranges from about 0.99 to about 0.95 and b ranges from about 0.01 to about 0.05. Also, a may range from about 0.95 to about 0.8 or from about 0.9 to about 0.8; also, b may range from about 0.05 to about 0.2 or from about 0.1 to about 0.2. These phosphors may be prepared by the vapor deposition methods discussed herein by starting with targets of CsBr, CsCl and EuCl₂ and controlling the deposition.

The phosphors prepared by the aforementioned methods exhibit substantially improved speed. Moreover, all samples of CsBr:Eu prepared with europium halides in the raw mixtures exhibited a blue photoluminescence (254 nm excitation) after firing with a power in Watt that is at least 100 times higher than the energy of a very weak red photoluminescence. Samples prepared with Eu₂O₃ as the starting material exhibited blue and red photoluminescence (254 nm excitation) after firing, wherein the power of the blue photoluminescence is substantially less than 100 times the energy of the red photoluminescence.

The phosphor produced by the methods described herein can beneficially be used in a powder panel wherein the phosphor is applied to a support from a solution containing a binder resin and the phosphor. Phosphor screens comprising a layer containing a phosphor embedded in a binder resin are well known in the art. In this case any binder known in the art can be used to form a screen or panel comprising a CsBr:Eu or CsBr_aCl_b:Eu phosphor according to the present invention. Suitable binders are, e.g., gelatin, polysaccharides such as dextrin, gum Arabic, and synthetic polymers such as polyvinyl butyl, polyvinyl acetate, nitrocellulose, ethylcellulose, vinylidene chloride-vinyl chloride copolymer, polyalkyl (meth)acrylate, vinyl chloride-vinyl acetate copolymer, polyurethane, cellulose acetate, cellulose acetate butyrate, polyvinyl alcohol, polystyrene, polyester, etc. These and other useful binders are disclosed e.g. in U.S. Patents 2,502,529, 2,887,379, 3,617,285, 3,300,310, 3,300,311 and 3,743,833. A mixture of two or more of these binders may be used, e.g., a mixture of polyethyl acrylate and cellulose acetobutyrate.

The weight ratio of phosphor to binder is generally within the range of from 50:50 to 99:1, preferably from 80:20 to 99:1. Preferably a self-supporting or supported layer of phosphor particles according to the present invention comprises said particles dispersed in a binding medium and a protective coating thereover characterized in that the binding medium substantially consists of one or more hydrogenated styrene-diene block copolymers, having a

saturated rubber block, as rubbery and/or elastomeric polymers. The polymer can be represented by the formula A-B-A (tri-block) or by the formula A-B (di-block), wherein A represents styrene and B represents the hydrogenated diene block, e.g., ethylene-butylene or ethylene-propylene. Further the ratio by volume of phosphor to binding medium is
5 preferably more than 70/30 and still more preferably more than 85/15.

The phosphor is especially well suited for manufacturing a "binderless" storage phosphor panel by physical vapor deposition comprising the deposition so as to have a "binderless" phosphor screen. Although any method for depositing a phosphor without a binder can be used to apply the cesium halide phosphor made by the method of this invention
10 (e.g., CsX:Eu or CsBr₂Cl₂:Eu) to a support, it is preferred to use a method selected from the group consisting of chemical vapor deposition or physical vapor deposition, including thermal vapor deposition, electron beam evaporation, magnetron sputtering, radio frequency sputtering and pulsed laser deposition or atomization techniques such as spray drying, thermal spraying, etc. Most preferably thermal vapor deposition is used to prepare binderless
15 screens containing a phosphor of this invention. The deposition of the phosphor according to this invention is preferably so that the CsX:Eu stimuable phosphor is present in the form of columnar crystals. Such panels have been disclosed in, e.g., EP-A-185 534, U.S. Patent No. 4,947,046, JP-A-61 245099, etc. In order to deposit a phosphor of this invention on a substrate by thermal vapor deposition, this phosphor is brought in to a heatable vessel. This
20 vessel and the substrate are brought in a deposition chamber that can be evacuated to at least 10⁻⁴ mbar. By adjusting the temperature of the vessel containing the phosphor and the evaporation time the thickness of the phosphor layer on the substrate can be adjusted.

A "binderless" storage phosphor panel containing a cesium halide phosphor can also be manufactured depositing simultaneously CsX and EuX'₂, EuX'₃ and/or EuOX', X being a
25 combination of Br and Cl in any ratio and X' being one or more halides. Thus the invention encompasses a method for manufacturing a phosphor screen containing a CsX:Eu stimuable phosphor, wherein X represents a halide selected from the group consisting of Br and Cl comprising the steps of:

- bringing multiple containers of said CsX and an Europium compound selected from
30 the group consisting of EuX'₂, EuX'₃ and EuOX', X' being one or more halide selected from the group consisting of F, Cl, Br and I in condition for vapor deposition and

- depositing, by a method selected from the group consisting of chemical vapor deposition or physical vapor deposition, including thermal evaporation, electron beam evaporation, magnetron sputtering, radio frequency sputtering and pulsed laser deposition or atomization techniques such as spray drying, thermal spraying, etc, both said CsX and said
5 Europium compound on a substrate in such a ratio that on said substrate a CsX phosphor, doped with between 10^{-3} mol % and 5 mol % of Europium, is formed.

The deposition can proceed from a single container containing a mixture of the starting compounds in the desired proportions. Thus the method encompasses further a method for manufacturing a phosphor screen containing a CsX:Eu stimuable phosphor,
10 wherein X represents one or more halides selected from the group consisting of Br and Cl comprising the steps of:

- mixing said CsX with between 10^{-3} and 5 mol % of an Europium compound selected from the group consisting of EuX'_2 , EuX'_3 and EuOX' , X' being one or more halide selected from the group consisting of F, Cl, Br and I

15 - bringing said mixture in condition for vapor deposition and
- depositing said mixture on a substrate by a method selected from the group consisting of chemical vapor deposition or physical vapor deposition, including thermal vapor deposition, electron beam evaporation, magnetron sputtering, radio frequency sputtering and pulsed laser deposition or atomization techniques such as spray drying,
20 thermal spraying, etc.

Bringing in condition for thermal vapor deposition means that the ingredients are brought in heatable containers and that these containers are placed, together with the substrate on which the phosphor has to be deposited in a deposition chamber that can be evacuated to at least 10^{-4} mbar. Generally, there are at least three possible embodiments: the starting
25 ingredients are mixed into a single heatable container, the starting ingredients are separated into individual heatable containers and the pre-formed CsX:Eu phosphor is placed into one or more heatable containers.

Support materials for storage screens, binderless as well as binder containing screens, containing a phosphor in accordance with the present invention, include cardboard, plastic
30 films such as films of cellulose acetate, polyvinyl chloride, polyvinyl acetate, polyacrylonitrile, polystyrene, polyester, polyethylene terephthalate, polyamide, polyimide, cellulose triacetate and polycarbonate; metal sheets such as aluminum foil and aluminum

alloy foil; ordinary papers; baryta paper; resin-coated papers; pigment papers containing titanium dioxide or the like; papers sized with polyvinyl alcohol or the like; and glass sheets. A plastic film is preferably employed as the support material for a binder containing screen; a glass or Al sheet is preferably employed as the support material for a binderless screen.

5 The plastic film may contain a light-absorbing material such as carbon black, or may contain a light-reflecting material such as titanium dioxide or barium sulfate. The former is appropriate for preparing a high-resolution type storage screen, while the latter is appropriate for preparing a high-sensitivity type storage screen.

10 Examples of preferred supports include polyethylene terephthalate, clear or blue colored or black colored (e.g., LUMIRROR C, type X30, (trade name) supplied by Toray Industries, Tokyo, Japan), polyethylene terephthalate filled with TiO_2 or with BaSO_4 . Metals such as e.g. aluminum, bismuth and the like may be deposited e.g. by vaporization techniques to get a polyester support having radiation-reflective properties.

15 These supports may have a thickness which may differ depending on the material of the support, and may generally be between 60 and 1000 μm , more preferably between 80 and 500 μm from the standpoint of handling.

EXAMPLES

MEASUREMENTS OF THE PROPERTIES OF THE PHOSPHORS:

20 The determination of the properties of the doped CsX crystals according to the present invention proceeded through following measurements:

25 -In a first measurement the "prompt" emission spectrum of the phosphor under X-ray excitation was measured. The measurement proceeds with a multichannel detector under excitation by X-ray irradiation and was carried out with an X-ray source operating at room temperature at 80 kVp and 15 mA. Under continuous X-ray excitation light of different wavelengths were produced. The rays of emission light, having different wavelengths, were collected and amplified in the different channels of the multichannel detector.

30 - In a second measurement the stimulation spectrum was determined. The light of a tungsten (quartz-iodine) lamp was fed into a monochromator (SPÉX 270M trade name of Yvon-Jobin, France) and then mechanically chopped with a rotating wheel with a single slit. The lamp provides a continuous spectrum extending from the near UV through the visible

spectrum into the infrared. The 520.24.33.0 grating from Yvon-Jobin was a 1200 line/mm grating covering the visible range from 350 nm to 1100 nm in the first order and was blazed at 750 nm. The wavelength of the stimulating light can be set via a step motor connected to the monochromator under the control of a computer. The second harmonic of the monochromator was eliminated by placing a 4 mm Schott GG435 filter in front of the phosphor screen, when the monochromator is set at a wavelength longer than 800 nm a RG 665 SCHOTT filter (trade name) was added. By chopping the stimulating light (duty cycle 1/200) only a small fraction of the absorbed energy in the phosphor was released. Only the AC signal was measured to eliminate the offset caused due to e.g. the dark current of the photomultiplier. A good signal to noise ratio was obtained by averaging several pulses. Upon completing the measurement the computer corrects the curve for the intensity wavelength dependence of the tungsten lamp and the diffraction efficiency of the grating

- In the third measurement the total photostimulable energy stored upon exposure to a given X-ray dose was determined. This property is expressed as "conversion efficiency" (C.E.):

Prior to X-ray excitation any residual energy still present in the phosphor screen was removed by irradiation with light of a 500 W quartz-halogen lamp. The phosphor screen was then excited with an X-ray source operating at 80 kVp and 5 mA. For that purpose the BALTEAUGRAPHE 2000 (tradename) X-ray source of Balteau, France was used. The low energy X-rays are filtered out with a 21 mm thick aluminum plate to harden the X-ray spectrum. After X-ray excitation the phosphor screen was transferred in the dark to the measurement set-up. In this setup laser light was used to photostimulate the X-ray irradiated phosphor screen. The laser used in this measurement was a diode laser emitting at 690 nm with a power of 5 mW. The diode laser was the type LT030-MD, trade name of Sharp, USA.

The laser-optics comprise an electronic shutter, a beam-expander and a filter. A photomultiplier (HAMAMATSU R 376) collects the light emitted by the photostimulation and gives a corresponding electrical current. The measurement procedure was controlled by a Hewlett Packard HP 382 (tradename) computer connected to a HP 6944 (tradename) multiprogrammer. After amplification with a current to voltage converter a TEKTRONIX TDS 420 (tradename) digital oscilloscope visualizes the photocurrent obtained. When the electronic shutter was opened the laser beam begins to stimulate the phosphor screen and the digital oscilloscope was triggered. Using a diaphragm placed in contact with the screen the light

emitted by only 7 mm^2 was collected. Approximately half of the laser power (2 mW) reaches the screen surface. In this way the intensity of the stimulating beam was more uniform.

The stimulating laser light (transmitted by the crystal) and the stimulated emission light are separated by a 6 mm BG 39 SCHOTT (trade name) filter, so that only the emitted light
5 reaches the photomultiplier.

The signal amplitude from the photomultiplier is linear with the intensity of the photostimulating light and with the stored photostimulable energy. The signal decreases with time. When the signal curve was entered the oscilloscope was triggered a second time to measure the offset which was defined as the component of error that was constant and
10 independent of inputs. After subtracting this offset the point at which the signal reaches $1/e$ of the maximum value was calculated. The integral below the curve was then calculated from the start to this $1/e$ point. The function was described mathematically by $f(t) = A \cdot e^{-t/\tau}$; wherein A is the amplitude, t is the time constant, τ is stimulation time, and e is the base number of natural logarithms.

15 The $1/e$ point is reached when $t = \tau$ at which 63 % of the stored energy has been released. To obtain said result, the computer multiplies the integral with the sensitivity of the system. The sensitivity of the photomultiplier and amplifier have therefore to be measured as a function of anode-cathode voltage of the photomultiplier and the convolution of the emission spectrum of the phosphor, the transmission spectrum of the 6 mm BG 39 SCHOTT (trade
20 name) filter and the wavelength dependence of the response of the photomultiplier have to be calculated. Because the emission light is scattered in all directions only a fraction of the emitted light is detected by the photomultiplier. The position of the panel and photomultiplier are such that 10 % of the total emission was detected by the photomultiplier. After all these corrections have been made a conversion efficiency value (C.E.) was obtained in $\text{pJ/mm}^2/\text{mR}$.

25

PREPARATION OF THE PHOSPHORS:

Basically all phosphors were prepared in the same way and only the nature and the amount of the activator (dopant) and the nature of the carrier gas were changed. The comparative CsBr:Eu phosphors were prepared by adding Eu_2O_3 to the CsBr before firing
30 and the invention CsBr:Eu phosphors were prepared by adding either EuCl_2 or EuBr_3 to the CsBr before firing. Also CsBr:Tl phosphors were prepared wherein the dopant was either

Tl₂O or one of TlBr or TlCl₃ • 4 H₂O. All chemicals were used as received from commercial suppliers, except for EuBr₃ and EuOBr. EuBr₃ was received in hydrated form from a commercial vendor and dried before preparing the CsBr:Eu phosphors of the present invention. Specifically, hydrated europium bromide was placed in a desiccator with desiccant and dried under vacuum for 24 hours. Despite such drying, it is possible that residual water was present and that the europium bromide was in a partially hydrated form. Moreover, given the hygroscopic nature of the materials involved, water may also become included in the europium bromide, in other starting materials and/or in the combined mixture during transfer and handling of such compounds or mixtures. The synthesis of EuOBr is described below.

Crystals of activated CsBr were prepared by mixing by manual grinding 20 g of 99.999% pure CsBr with the activator compound in the right proportion (see Table 1, below). The mixture was placed in an Al₂O₃ crucible and placed in the quartz tube of a tube furnace. The quartz tube was sealed with a flange with water lock and flushed with carrier gas prior to firing and during the firing process. The gas flow rate was 120 cc/min. The carrier gas was either nitrogen or, alternatively, Ar (with 5.8 mol % H₂), and is indicated in Table 1, below for particular examples.

The furnace temperature was increased from room temperature to 43 °C at a rate of 5 °C/min. Dwell time at this temperature was 6 hours. Next, the temperature was ramped to 700 °C at 10 °C/min. Dwell time at 700 °C was 5 min. The furnace was cooled to room temperature at 10 °C/min.

The crucible containing the phosphor was removed from the furnace and the crucible was broken to set the phosphor crystals free. Larger crystalline particles were selected and polished to a thickness of ca. 500 µm for measurement.

In the following Table 1 the starting materials for the synthesis of the comparative phosphors and invention phosphors are given, as well as their conversion efficiency (CE).

Preparation of EuOBr:

7.0 g (0.02 mol) of Eu₂O₃ was slowly added to a reactor containing 50 ml of deionised water and 22.4 g (0.13 mol) of a 47% HBr solution. Next, 3.9 g (0.004 mol) of NH₄Br was added. The solution was heated to 60°C and stirred until a clear, colourless solution was obtained.

Next, the solution was evaporated to dryness. To this aim, it was poured in a quartz container and placed in a sealed quartz tube. Before heating, the quartz tube was flushed with pure N₂ for 15 minutes.

For drying under N₂ flow the following temperature programme was used:

- 5 -starting temperature: 120°C,
- dwell time at 120°C: 3 hours,
- rise-time from 120 to 300°C: 2 hours,
- dwell time at 300°C: 12 hours,
- rise-time from 300 to 480°C: 15 minutes,
- 10 -dwell time at 480°C: 2 hours.

After drying, the tube was allowed to cool for 1 hour. The resulting powder was slightly yellowish and showed the characteristic Eu²⁺ emission under 254 nm excitation. Nevertheless, XRD analysis, the Eu/Br ratio determined via ICP-OES and ionchromatography, showed that the resulting product was almost pure EuOBr.

15

Comparative example phosphors:

The comparative example phosphors were prepared by adding Eu₂O₃ to CsBr.

- Crystals of activated CsBr were prepared by mixing by manual grinding ca. 20 g of 99.999% pure CsBr with the activator compound in the right proportion. The mixture was placed in an
- 20 Al₂O₃ crucible and placed in the quartz tube of a tube furnace. The quartz tube was sealed with a flange with oil lock and flushed with the 5.8 mol % H₂ in Ar carrier gas prior to firing and during the firing process. The gas flow rate was 120 cc/min. The furnace temperature was increased from room temperature to 43 °C at a rate of 5 °C/min. Dwell time at this temperature was 6 hours. Next, the temperature was ramped to 700 °C at 10 °C/min. Dwell
- 25 time at 700 °C was 5 min. The furnace was cooled to room temperature at 10 °C/min. The crucible containing the phosphor was removed from the furnace, cooled and the phosphor crystals were taken from the crucible. Larger crystalline particles were selected and polished to a thickness of ca. 500 µm for measurement.

- The conversion efficiency of the reference BaF(Br,I):Eu phosphor was measured
- 30 under stimulation with a He-Ne laser and using a BG-3 (6mm) filter to separate the emission end stimulation light.

Table 1

Sample NR.	Dopant	Concentration of Eu vs. Cs (mol %)	Phosphor composition	Carrier gas	C.E. pJ/mm ² /mR
Reference			BaF(Br,I):Eu		57
Comp. Example 1	Eu ₂ O ₃	10 ⁻³	CsBr:Eu	Ar/H ₂	2.1
Comp. Example 2	Eu ₂ O ₃	10 ⁻²	CsBr:Eu	Ar/H ₂	5
Comp. Example 3	Eu ₂ O ₃	10 ⁻¹	CsBr:Eu	Ar/H ₂	1.9
Comp. Example 4	Eu ₂ O ₃	3.10 ⁻¹	CsBr:Eu	Ar/H ₂	1.4
Comp. Example 5	Eu ₂ O ₃	1	CsBr:Eu	Ar/H ₂	12
Comp. Example 6	Eu ₂ O ₃	3	CsCl:Eu	Ar/H ₂	11
Example 7	EuCl ₂	10 ⁻³	CsBr:Eu	Ar/H ₂	2.1
Example 8	EuCl ₂	10 ⁻²	CsBr:Eu	Ar/H ₂	13
Example 9	EuCl ₂	10 ⁻¹	CsBr:Eu	Ar/H ₂	27
Example 10	EuCl ₂	3.10 ⁻¹	CsBr:Eu	Ar/H ₂	56
Example 11	EuCl ₂	1	CsBr:Eu	Ar/H ₂	101
Example 12	EuCl ₂	3	CsBr:Eu	Ar/H ₂	37
Example 13	EuCl ₂	10 ⁻³	CsBr:Eu	N ₂	4.6
Example 14	EuCl ₂	10 ⁻²	CsBr:Eu	N ₂	15
Example 15	EuCl ₂	3.10 ⁻¹	CsBr:Eu	N ₂	110
Example 16	EuBr ₃	10 ⁻³	CsBr:Eu	Ar/H ₂	4.6
Example 17	EuBr ₃	10 ⁻²	CsBr:Eu	Ar/H ₂	22
Example 18	EuBr ₃	10 ⁻¹	CsBr:Eu	Ar/H ₂	23.4
Example 19	EuBr ₃	3.10 ⁻¹	CsBr:Eu	Ar/H ₂	137
Example 20	EuBr ₃	1	CsBr:Eu	Ar/H ₂	124
Example 21	EuBr ₃	3	CsBr:Eu	Ar/H ₂	53
Comp. Example 22	Tl ₂ O ₃	3.10 ⁻¹	CsBr:Tl	Ar/H ₂	0.077
Comp. Example 23	TlCl ₃	3.10 ⁻¹	CsBr:Tl	Ar/H ₂	0
Comp. Example 24	TlBr ₃	3.10 ⁻¹	CsBr:Tl	Ar/H ₂	0
Comp. Example 25	Tl ₂ O ₃	3.10 ⁻¹	CsBr:Tl	N ₂	0.154
Example 26	EuOBr	10 ⁻²	CsBr:Eu	Ar/H ₂	30

Example 27:

A film of cesium bromide doped with europium chloride was deposited simultaneously on quartz and silicon substrates. The substrate for deposition consisted of a

three-inch quartz wafer. A three-inch diameter semicircular silicon substrate was attached to one half of the quartz wafer. Phosphors CsBr:EuCl_2 ($[\text{Eu}] = 1 \text{ mol\% vs Cs}$) were prepared as described for example 11. The film of cesium bromide doped with europium was prepared by the thermal evaporation of the phosphor samples in a deposition chamber operating at a pressure of approximately 8×10^{-6} mbar. Chunks of the bulk phosphor were loaded into three separate evaporation crucibles (alumina) in the chamber. After evacuation of the chamber, the three crucibles were simultaneously heated to 550°C . Deposition was initiated on the substrates facing the crucibles by opening a flag placed between the crucibles and the substrate. The orientation of the evaporation crucibles with respect to the substrate was such that a film of even thickness was deposited over the predefined substrate area. The deposition rate from each crucible was approximately 60 \AA/sec and was monitored using quartz crystal monitors. The distance between the substrate and the evaporation crucibles was 15 inches. The quartz and silicon substrates were subsequently removed from the chamber and a protective layer of aluminum oxide (1000 \AA) deposited over the film on the substrates using r.f. magnetron sputtering. The final thickness of the film was approximately $30 \text{ }\mu\text{m}$ as measured by profilometry. Blue emission was observed from the film by illuminating the sample with ultraviolet light (254 nm). The photoluminescence spectrum is shown in Figure 4. Conversion Efficiency = $19.3 \text{ pJ/mm}^2/\text{mR}$.

The luminescence spectrum was measured from the europium doped cesium bromide film on the silicon substrate using Spex (TRADENAME) double monochromators for the photoexcitation wavelength (280 nm) and to disperse the resulting luminescence which was detected by a spectrally corrected photomultiplier.

It is to be understood that the above description is intended to be illustrative and not restrictive. Many embodiments will be apparent to those of skill in the art upon reading the above description. The scope of the invention should therefore be determined not with reference to the above description, but should instead be determined with reference to the appended claims, along with the full scope of equivalents to which such claims are entitled. The disclosures of all articles, patents and references, including patent applications and publications, are incorporated herein by reference for all purposes.

WHAT IS CLAIMED IS:

- 1 1. A method for producing a CsX:Eu stimuable phosphor, wherein X represents a halide
2 selected from the group consisting of Br, Cl and combinations thereof, comprising the
3 steps of:
4 - mixing CsX with an Europium compound selected from the group consisting of
5 EuX'_2 , EuX'_3 and EuOX' , X' being selected from the group consisting of F, Cl, Br, I and
6 combinations thereof,
7 - heating said mixture at a temperature above 450 °C
8 - cooling said mixture, and
9 - optionally recovering the CsX:Eu phosphor..
- 1 2. A method according to claim 1, wherein between 10^{-3} and 5 mol % of said Europium
2 compound is mixed with said CsX.
- 1 3. A method according to claim 1, wherein between 10^{-1} and 3 mol % of said Europium
2 compound is mixed with said CsX.
- 1 4. A method according to claim 1, wherein X' is a member selected from the group
2 consisting of Cl and Br.
- 1 5. A method according to claim 2, wherein X' is a member selected from the group
2 consisting of Cl and Br.
- 1 6. A method according to claim 3, wherein X' is a member selected from the group
2 consisting of Cl and Br.
- 1 7. A binderless phosphor screen containing a CsX:Eu phosphor prepared according to claim
2 1.
- 1 8. A binderless phosphor screen containing a CsX:Eu phosphor prepared according to claim
2 2.
- 1 9. A binderless phosphor screen containing a CsX:Eu phosphor prepared according to claim
2 3.

- 1 10. A binderless phosphor screen containing a CsX:Eu phosphor prepared according to claim
2 4.
- 1 11. A binderless phosphor screen containing a CsX:Eu phosphor prepared according to claim
2 5.
- 1 12. A binderless phosphor screen containing a CsX:Eu phosphor prepared according to claim
2 6.
- 1 13. A method for producing a binderless phosphor screen comprising the steps of
2 - producing a CsX:Eu phosphor with the method of claim 1 and
3 - depositing said phosphor on a substrate by a method selected from the group
4 consisting of physical vapor deposition, chemical vapor deposition or an atomization
5 technique.
- 1 14. A method for manufacturing a binderless phosphor screen on a substrate containing a
2 CsX:Eu stimutable phosphor, wherein X represents a halide selected from the group
3 consisting of Br, Cl and combinations thereof comprising the steps of :
4 - bringing heatable multiple containers of CsX and an Europium compound selected
5 from the group consisting of EuX'_2 , EuX'_3 and EuOX' , X' being selected from the group
6 consisting of F, Cl, Br, I and combinations thereof together with the substrate in a
7 deposition chamber that is evacuated to at least 10^{-4} mbar; and
8 - depositing, by a method selected from the group consisting of physical vapor
9 deposition, chemical vapor deposition or atomization technique, both said CsX and said
10 Europium compound on a substrate in such a ratio that on said substrate a CsX phosphor,
11 doped with between 10^{-3} and 5 mol % of Europium, is formed.
- 1 15. A method for manufacturing a phosphor screen containing of a CsX:Eu stimutable
2 phosphor, wherein X represents a halide selected from the group consisting of Br and Cl
3 comprising the steps of :
4 - mixing CsX with between 10^{-3} and 5 mol % of an Europium compound selected
5 from the group consisting of EuX'_2 , EuX'_3 and EuOX' , X' being selected from the group
6 consisting of F, Cl, Br, I and combinations thereof,

- 7 - bringing said mixture in a container and bringing this container together with the
8 substrate in a deposition chamber that is evacuated to at least 10^{-4} mbar and
9 - depositing said mixture on a substrate by a method selected from the group
10 consisting of physical vapor deposition, chemical vapor deposition or atomization
11 technique.

- 1 16. A method for recording and reproducing images of objects made by high energy
2 radiation comprising:
3 - exposing a panel with X-ray radiation, said panel comprising a CsX:Eu stimuable
4 phosphor, wherein X represents a halide selected from the group consisting of Br, Cl and
5 combinations thereof, including between 10^{-3} and 5 mol% of an Europium dopant, said
6 dopant originating from an Europium compound selected from the group consisting of
7 EuX'_2 , EuX'_3 and EuOX' , X' being selected from the group consisting of F, Cl, Br, I and
8 combinations thereof,
9 - stimulating said panel with radiation having a wavelength between 500 nm and 1100
10 nm thereby releasing stimulated radiation and
11 - collecting said stimulated radiation.

- 1 17. A phosphor of the formula $\text{CsBr}_a\text{Cl}_b\text{:Eu}$ where $a + b = 1$, and a ranges from about 0.99 to
2 about 0.8 and b ranges from about 0.01 to about 0.2.

- 1 18. The phosphor of claim 14, wherein a ranges from about 0.99 to about 0.95 and b ranges
2 from about 0.01 to about 0.05.

- 1 19. The phosphor of either claim 14 or 15, wherein the phosphor is an x-ray storage
2 phosphor.

- 1 20. A CsX:Eu compound prepared according to either of the methods of claims 1, 2, 3, 4, 5
2 or 6.

- 1 21. A phosphor characterised by the formula CsX:Eu , wherein X is selected from the group
2 consisting of Br, Cl and combinations thereof and said phosphor exhibiting, when
3 excited with radiation of 254 nm, a blue photoluminescence and a red
4 photoluminescence wherein said blue photoluminescence has an power (Watt) at least
5 100 times higher than said red photoluminescence.

- 1 22. The phosphor of claim 21, wherein X is Br.
- 1 23. A binderless phosphor screen comprising a CsX:Eu stimuable phosphor according to
2 claim 21.
- 1 24. A binderless phosphor screen comprising a CsX:Eu stimuable phosphor, according to
2 claim 22.

Fig. 1/4

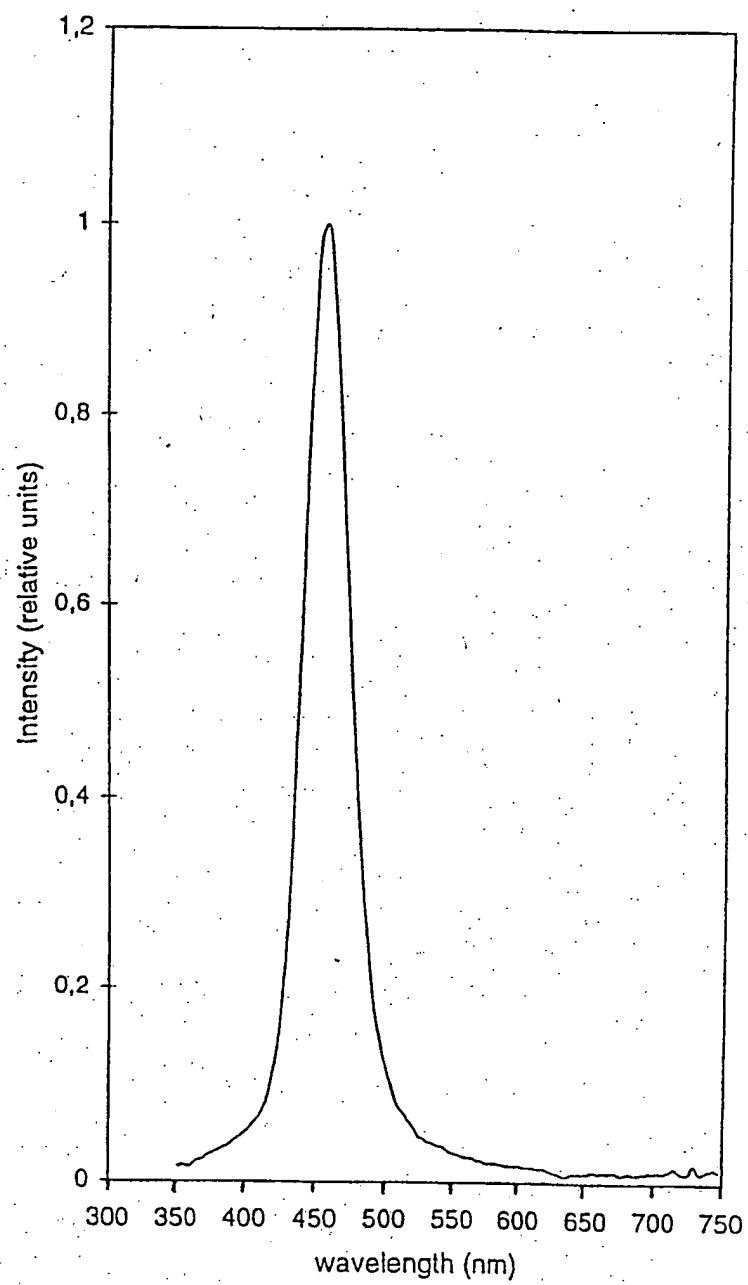


FIG. 1

Fig. 2/4

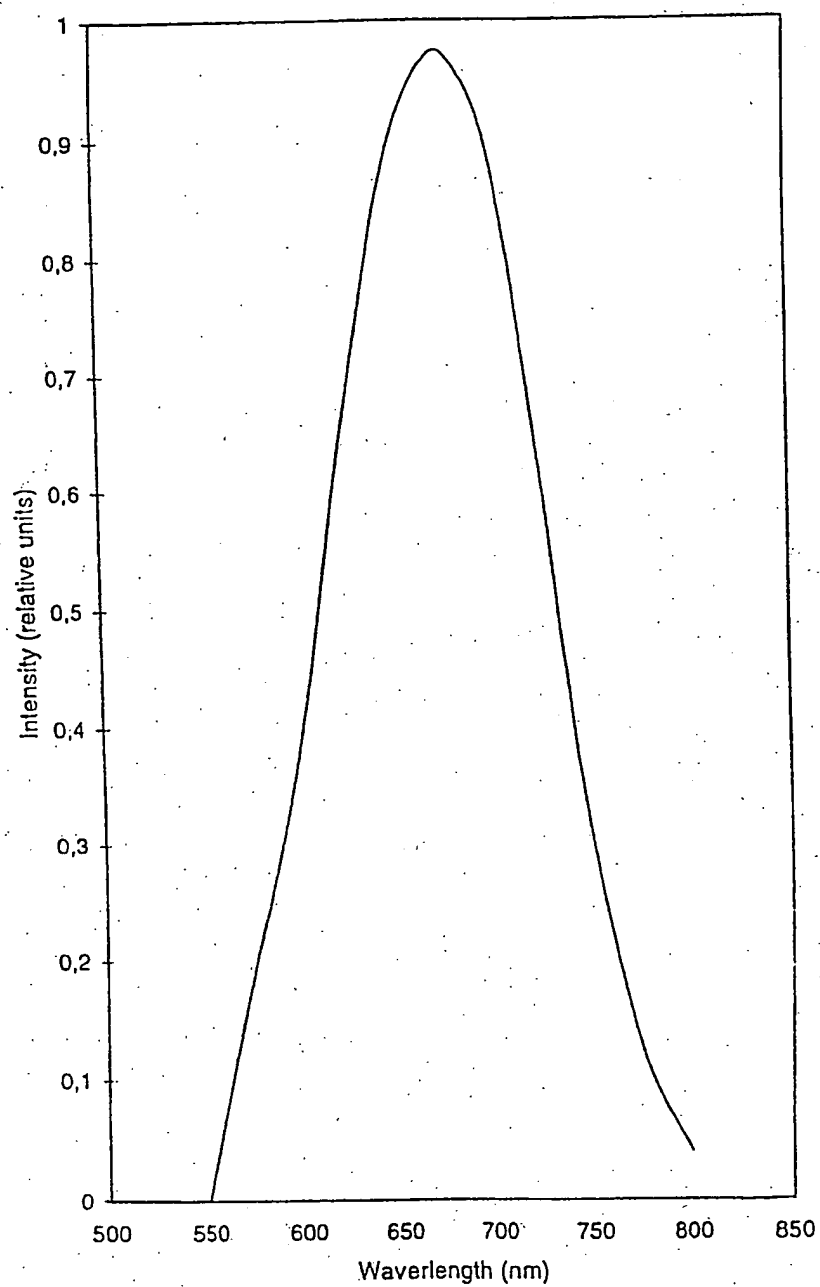


FIG 2

Fig. 3/4

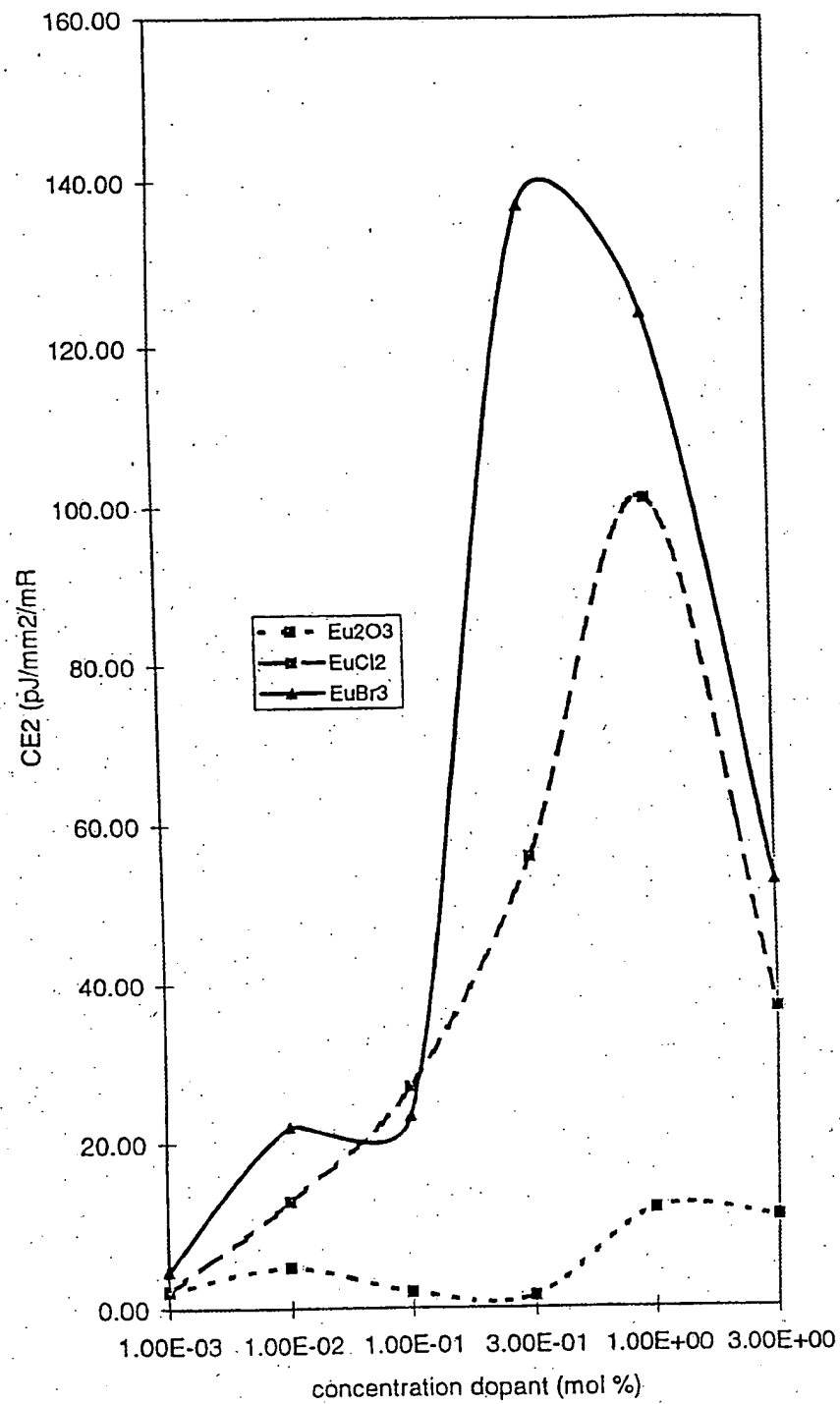


FIG. 3

4/4

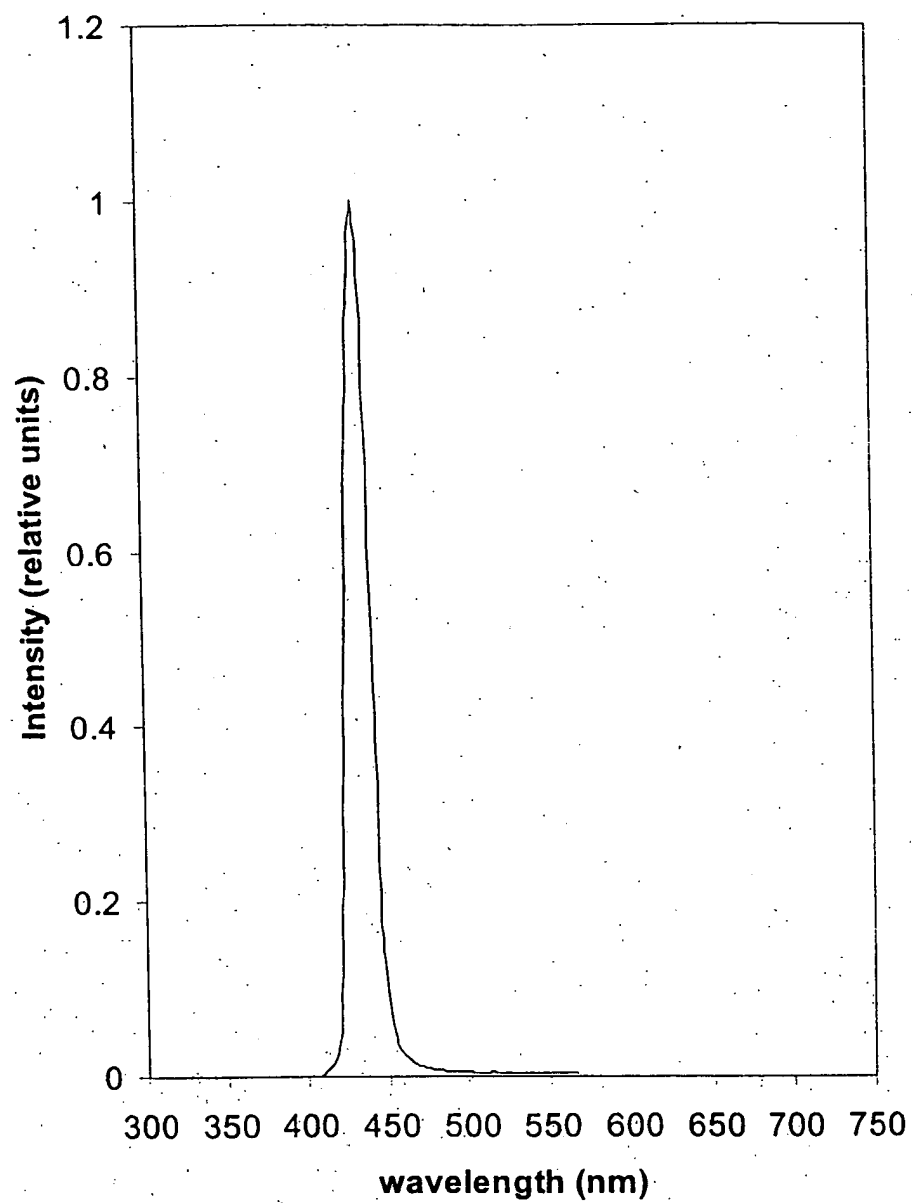


Fig. 4

INTERNATIONAL SEARCH REPORT

Inte Application No

PC1/US 00/16904

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01J9/22 G21K4/00 C09K11/85

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09K H01J G21K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, INSPEC, WPI Data, PAJ, IBM-TDB, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 780 376 A (NAKAMURA TAKASHI) 25 October 1988 (1988-10-25) the whole document	1-24
A	PEDRERO N E ET AL: "Analysis of the optical behaviour of Eu/sup 2+/ ions in CsCl crystals" PHYSICA STATUS SOLIDI B, 1 OCT. 1997, AKADEMIE VERLAG, GERMANY, vol. 203, no. 2, pages 591-598, XP000912179 ISSN: 0370-1972 page 591 -page 598	17,21

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- *G* document member of the same patent family

Date of the actual completion of the international search

28 September 2000

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09/10/2000

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Initial Application No

PCT/US 00/16904

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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